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INCORPORATION OF A CHEMICAL EQUILIBRIUM EQUATION OF STATE INTO LOCI-CHEM

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Introduction

Renewed interest in development of advanced high-speed transport, reentry vehicles and propulsion systems has led to a resurgence of research into high speed aerodynamics. As this flow regime is typically dominated by hot reacting gaseous flow, efficient models for the characteristic chemical activity are necessary for accurate and cost effective analysis and design of aerodynamic vehicles that transit this regime. The LOCI-Chem code recently developed by Ed Luke at Mississippi State University for NASA/MSFC and used by NASA/MSFC and SSC represents an important step in providing an accurate, efficient computational tool for the simulation of reacting flows through the use of finite-rate kinetics [3]. Finite rate chemistry however, requires the solution of an additional N-1 species mass conservation equations with source terms involving reaction kinetics that are not fully understood. In the equilibrium limit, where the reaction rates approach infinity, these equations become very stiff. Through the use of the assumption of local chemical equilibrium the set of governing equations is reduced back to the usual gas dynamic equations, and thus requires less computation, while still allowing for the inclusion of reacting flow phenomenology.

The incorporation of a chemical equilibrium equation of state module into the LOCI-Chem code was the primary objective of the current research. The major goals of the project were: (1) the development of a chemical equilibrium composition solver, and (2) the incorporation of chemical equilibrium solver into LOCI-Chem. Due to time and resource constraints, code optimization was not considered unless it was important to the proper functioning of the code.

Procedure for the Determination of Equilibrium Properties

The primary objective was accomplished through the modification and incorporation of a "black box" chemical equilibrium solver for the determination of the equilibrium composition and thus thermodynamic properties of the reacting flow. This “black box” solver was written in a generic fashion to solve any arbitrary mixture of thermally perfect gases. Unlike curvefits of equilibrium properties which are limited to the specific mixture the empirical data was collected for, the methodologies can be applied to any reacting flow given a few reference thermodynamic properties [3]. The equilibrium composition solver solves a set of nonlinear governing equations comprising NS-NE laws of mass action,

$$w_i(\rho_j, T) = \sum_{r=1}^{NR} \left(\nu''_{i,r} - \nu'_{i,r}\right) \left[K_{c,r} \prod_{s=1}^{NS} \left(\frac{\rho_s}{M_s}\right)^{\nu'_{s,r}} - \prod_{s=1}^{NS} \left(\frac{\rho_s}{M_s}\right)^{\nu''_{s,r}} \right], i = 1, NS - NE$$

NE elemental mass constraints,

$$w_{NS\text{-}NE+i}(\rho_j) = \sum_{s=1}^{NS} \frac{\alpha_{i,j}}{M_j} \frac{\rho_j}{\rho} - \left[\sum_{s=1}^{NS} \frac{\alpha_{i,j}}{M_j} \frac{\rho_j}{\rho} \right]_{t=0}, i = 1, NE$$

and either the caloric equation of state

$$d(\rho_j, T) = (\rho e)_{t=0} - \sum_{j=1}^{NS} \rho_j \left[\int_{T_{ref}}^{T} c_{v_j}(\tau) d\tau + e_{f_j} \right]$$

or the thermal equation of state

$$d(\rho_j, T) = (p)_{t=0} - \sum_{j=1}^{NS} \rho_j R_j T$$

for NS species mass fractions and an additional dependent variable, where NR, NE and NS represent the number of reactions, elements and species, respectively. The assumption of local chemical equilibrium means that the complete thermodynamic state can be determined through the specification of two state variables, specifically for the purposes of the current work as either a function of density and internal energy, pressure and density, or pressure and temperature. The caloric equation of state is used for the first situation, and the thermal equation of state for the latter two. The additional dependent variable is temperature for the first two cases and global density for the state as a function of pressure and temperature. Newton's method is employed to linearize the governing equations which are then iterated upon until convergence is achieved.

Upon convergence, the complete equilibrium composition is known via the species densities as well as the temperature. Through application of the standard mixture rules, various thermodynamic properties can be obtained: internal energy, enthalpy, gas constant, pressure, etc. Further by reusing the Jacobians utilized during the solution process, partial derivatives of species mass fractions with respect to density and temperature can be obtained. These can then be used to determine other properties of interest, such as the equilibrium isentropic index and hence equilibrium speed of sound. Full details of these procedures can be found in [1].

Coupling to the flow solver, simply requires the incorporation of the equilibrium equation of state module into LOCI-Chem. Whenever thermodynamic properties are required, the flow solver simply calls for the state defined as a function of either internal energy and density, pressure and density, or pressure temperature. The complete thermodynamic state is provided as a c++ object and can be queried for the desired properties. In addition to the thermodynamic properties, special derivatives of pressure and specific energy per unit volume with respect to density and pressure are provided for the flux computation.

Results for the Composition Solver

In order to access the accuracy of the techniques used for the determination of the equilibrium properties, comparisons were made of results to theoretical and empirical data. Specifically, the validation study involved the determination of properties for a 17-species air model, with comparisons of both equilibrium composition and thermodynamic properties for a number of densities ranging from $1/10000^{th}$ to 100 atmospheres, where atmospheric density would be 1.293 kg/m^3. A composition plot for the case at approximately 100 atmospheres is presented in Figure 1(a) as seen on the next page. As can be seen there is excellent agreement with the theoretical results up to a temperature of about 8000K. This is the point at which the mixture is beginning to ionize. The particular thermodynamic model employed for the species internal energy is a simple vibrational model whereby ionization energy is not accounted for and hence the discrepancy. Figure 1(b) shows pressure profiles at constant density as functions of temperature. Comparisons are made to values obtained from the empirical curve fits of Tannehill, et al [5]. Again there is excellent agreement up to the point at which ionization

becomes important. Similar results were obtained for other densities and thermodynamic properties. The capability of the equilibrium solver to handle arbitrary mixtures was demonstrated by obtaining solutions of equilibrium composition and thermodynamic properties using a 6-species hydrogen-oxygen combustion model, the results of which are not shown.

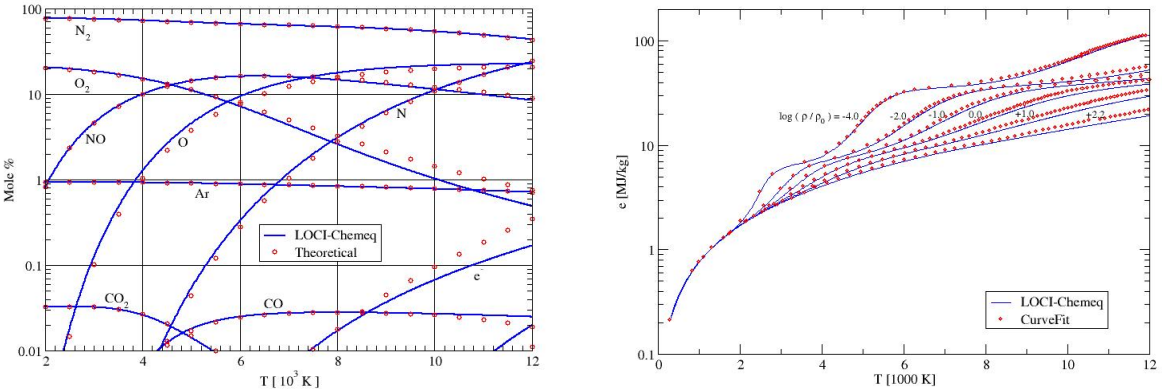

Figure 1: 17-Species Air Results (a) Composition for 100 Atmospheres, and (b) Internal Energy vs. Temperature

Shocktube Solution

After incorporating the chemical equilibrium equation of state module into LOCI-Chem a demonstration of its effectiveness and utility was desired. This was accomplished by investigating a simple shocktube problem where the left state was defined with a pressure of 1 MPa and density of 1.00 kg/m^3 and the right state was defined with a pressure of 100 kPa and 1.00 kg/m^3. Results of the shocktube problem are represented with the evolution of temperature as presented in Figure 2. Looking at the shock wave propagating to the right, it is easy to

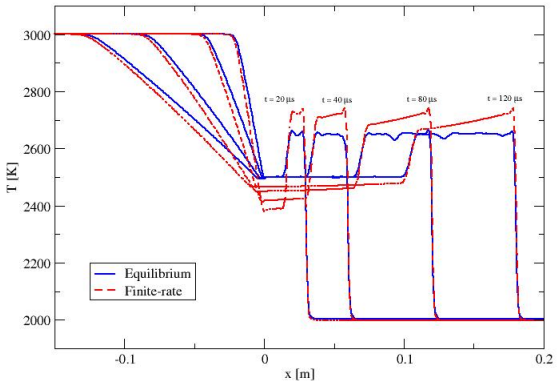

Figure 2: Evolution of Temperature for the Shocktube Problem

recognize the finite-rate values jumping up to the frozen limit and as time progresses, the shock propagates, the temperature relaxes to the equilibrium solution. This is a well known physical phenomenon representing the fact that the kinetic energy created across the shock is first converted to thermal energy and then relaxes through chemical energy to the equilibrium limit.

Further Work

Results obtained using the chemical equilibrium solver were promising and there was good agreement with theoretical and empirical data. However, there were some problems that were noticed. While the finite-rate solution for the shocktube problem required only minutes, the equilibrium solution required hours. This can be attributed to the lack of good initial guesses passed to the equilibrium composition solver caused by the lack of a mechanism to save mass fractions and temperature values from previous iterations in LOCI-Chem. This problem needs to be addressed in future work. Particular remedies include retaining previous composition information or even hints towards a good initial starting point based upon ranges of values.

Conclusions

A chemical equilibrium equation of state module has been added to LOCI-Chem. This module provides a less computationally expensive alternative to finite-rate chemistry while still providing the capability of modeling reacting flows. This solution methodology has proven to be accurate, though not necessarily efficient at this point.

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